JC07 Rec'd PCT/PTO 05 MAR 2002

FORM PTO-1390 U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE
(REV 11-2000)

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. § 371

ATTORNEY'S DOCKET NUMBER

204552022500

U S. APPLICATION NO (If known, see 37 CFR 1 5)

10/070292 to be assigned

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/04491	July 6, 2000	Yes

TITLE OF INVENTION

PRETREATMENT METHOD FOR ELECTROLESS PLATING

APPLICANT(S) FOR DO/EO/US

Hirokazu TANAKA, Satoshi HIRONO, Hiroyuki NIINO, Akira YABE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))

Items 11. to 16. below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☒ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☒ A copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

   request for Rectification of Obvious Error, PCT/IB/306; return receipt postcard.

CERTIFICATE OF HAND DELIVERY

I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on March 5, 2002.

Norman Slaveter

N. Slaveter

dc-305195 v1

JC19 Rec'd PCT/PTO 05 MAR 2002

U.S. APPLICATION NO (if known, see 37 CFR 1.5) to be assigned 10/070292	INTERNATIONAL APPLICATION NO PCT/JP00/04491	ATTORNEY'S DOCKET NUMBER: 2045520225

21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

CALCULATIONS PTO USE ONLY

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO $1,040.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provision of PCT Article 33(1)-(4) $710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =				$890	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total claims	1\4 - 20 =	0	x $18.00	$	
Independent claims	1 - 3 =	0	x $84.00	$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	$280	
TOTAL OF ABOVE CALCULATIONS =				$280	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by ½.				$	
SUBTOTAL =				$1,170	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$1,170	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00 per property** +				$40.00	
TOTAL FEES ENCLOSED =				$1,210	
				Amount to be refunded:	$
				charged:	$*

a. ☐ A check in the amount of $ to cover the above fees is enclosed.

b. ☒ Please charge my **Deposit Account No. 03-1952**, referenceing **204552022500** in the amount of $1,210.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees that may be required, or credit any overpayment to **Deposit Account No. 03-1952**. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Barry E. Bretschneider
Morrison & Foerster LLP
2000 Pennsylvania Avenue, N.W.
Washington, D.C. 20006-1888

SIGNATURE

Barry E. Bretschneider
Registration No. 28,055 Date: March 5, 2002

PATENT
Docket No. 204552022500

CERTIFICATE OF HAND DELIVERY
I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on March 5, 2002.

Norma Slaveter

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of: Hirokazu TANAKA *et al.*	Examiner: Not Yet Assigned
Serial No.: Not Yet Assigned	Group Art Unit: Not Yet Assigned
Filing Date: Concurrently Herewith	
For: PRETREATMENT METHOD FOR ELECTROLESS PLATING	

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to the calculation of the filing fee for this application, please enter the following amendments:

AMENDMENTS

In the Specification:

Replace the specification with the attached substitute specification.

In the Claims:

Amend claims 1-8 to read as follows:

1. (Amended) A pretreatment method for electroless plating, comprising:

adding an inorganic filler to a polymeric material;

molding the material to obtain a polymeric mold;

irradiating the mold with a laser; and

immersing the mold in a noble metal aqueous solution.

2. (Amended) The pretreatment method for electroless plating according to claim 1, wherein 10-50 weight % of the inorganic filler is added.

3. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein a total energy inputted by the laser to the mold is 10-500 J/cm^2 .

4. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein the laser is irradiated on an area of the mold so that a fluence and the number of times of irradiation are set to obtain a charging state suitable for precipitating noble metal on the irradiated area.

5. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein the polymeric material is selected from the group consisting of a liquid crystal polymer, polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, ABS, polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone, polyimide, epoxy resin and composite resins thereof.

6. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein the polymeric material comprises two or more kinds of resins having different laser ablation threshold values.

7. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein a palladium aqueous solution is used as the noble metal aqueous solution.

8. (Amended) The pretreatment method for electroless plating according to claim 1 or 2, wherein a glass filler is used as the inorganic filler.

REMARKS

Applicants have provided a substitute specification and amended the abstract to put them in more conventional form for examination. No new matter has been added in the substitute specification. Applicants have also amended the claims to eliminate improper multiple dependent claims and to improve their language without affecting claim scope.

Entry of these amendments and early action allowing claims 1-8 are solicited.

Attached hereto is a marked-up version of the changes made to the specification and claims by this amendment, captioned "**Version with markings to show changes made**".

In the event that the transmittal letter is separated from these documents and the Patent and Trademark Office determines that an extension and/or other relief is required, applicants petition for any required relief including extensions of time and authorizes the Commissioner to charge the cost of such petitions and/or other fees due in connection with the filing of these documents to **Deposit Account No. 03-1952**, Ref. 204552022500.

Dated: March 5, 2002

Respectfully submitted,

Barry E. Bretschneider
Registration No. 28,055

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Facsimile: (202) 263-8396

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

Amend the abstract as follows:

ABSTRACT OF THE DISCLOSURE

An inorganic filler is added to a polymeric material. An obtained polymeric mold is irradiated with a laser and immersed in ~~an anionic~~ **a** noble metal aqueous solution and thereafter electroless plating is performed.

Amend the specification as follows:

~~DESCRIPTION~~

PRETREATMENT METHOD FOR ELECTROLESS PLATING

BACKGROUND OF THE INVENTION

Field of the Invention: ~~**TECHNICAL FIELD**~~

The present invention relates to a pretreatment method for electroless plating.

~~**BACKGROUND ART**~~ **Description of the Related Art:**

In general, a surface of a mold composed of a polymeric material is roughened by chemicals, palladium is adsorbed therein and then the mold is subjected to electroless plating. However, since adsorption of palladium alone is difficult, a tin-palladium compound is adsorbed and then reduced.

Surface roughening by using chemicals cannot be selectively performed. When only a prescribed region is plated, the whole surface is once plated and then exposure and development need to be performed by using a photoresist. Therefore, a method by which a surface of a polymeric mold can be easily plated is being required.

As described in Japanese ~~Patent~~ Unexamined **Patent** Publication No. Hei 4-183873, a method by which a prescribed region can be plated by irradiating a mold composed of a polymeric material with ultraviolet laser beams was proposed.

According to this method, only a prescribed region can be plated ~~only~~ by irradiating with an ultraviolet laser, immersing in a palladium colloidal aqueous solution and then performing electroless plating. That is, since only an irradiated region is positively charged by the irradiation with an ultraviolet laser, palladium colloid can be easily attached to only the irradiated region when the mold is immersed in an anionic noble metal aqueous solution. Only palladium, which is a catalyst of electroless plating, can be deposited by allowing the aqueous solution to contain a reducing agent therein.

However, this method ~~by~~ **using** laser irradiation has the following problems and is not employed currently.

~~That is~~ **First**, since only the periphery of the irradiated region (prescribed region) is charged when the laser having a high fluence is irradiated **onto it**, irradiation of a low fluence needs to be performed. However, a sufficient quantity of charge is not obtained with such irradiation and thereby palladium colloid is not sufficiently attached. A substantial amount of laser beams need to be irradiated and ~~operatability~~ **operability** is deteriorated. Specifically, when a laser having a low fluence of 0.05 J/cm^2 /pulse is irradiated, the number of times of irradiation needs to be 1000 to obtain a sufficient charge quantity.

Also, when a laser having a low fluence is irradiated, surface irregularities of the irradiated region become small and thereby formed plating is easily peeled.

Furthermore, a charging phenomenon by irradiation of a low fluence is unique to ~~an~~ **the** ultraviolet laser and ~~thereby~~ **therefore** selectable equipment is limited.

Accordingly, ~~an object~~ **a feature** of the present invention is to provide a pretreatment method for electroless plating by which a prescribed region can be efficiently and firmly plated irrespective of the kind of a laser.

~~DISCLOSURE~~ SUMMARY OF THE INVENTION

The present inventors found that the main cause of charging of a mold surface by laser irradiation was removed and scattered substances (hereinafter, referred to as debris) generated by abrasion. Also, the present inventors found that these debris could be prevented from scattering by allowing the mold to contain an inorganic filler.

According to the present invention, a pretreatment method for electroless plating as means for solving the aforementioned problems is provided such that an inorganic filler is added to a polymeric material and an obtained polymeric mold is irradiated with a laser and immersed in ~~an anionic~~ **a** noble metal aqueous solution.

With this ~~constitution~~ **arrangement**, the added inorganic filler generates a sufficient quantity of charged debris upon laser irradiation irrespective of the level of the fluence and the debris are prevented from scattering outside the irradiated region. Therefore, when the mold is immersed in ~~an anionic~~ **a** noble metal aqueous solution, noble metal can ~~be attached~~ **attach** only to a laser irradiated region. As a result, when electroless plating is performed, noble metal attached to the laser irradiated region acts as a catalyst and thereby a favorable plating film can be formed on a desired site (irradiated region).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a state of an irradiated region depending on the fluence and the number of times of irradiation.

~~BEST MODE FOR CARRYING OUT~~ DETAILED DESCRIPTION OF THE INVENTION

An embodiment of the pretreatment method for electroless plating according to the present invention is described below.

In this pretreatment method for electroless plating, an inorganic filler is added to a polymeric material and ~~an~~ **the mold** obtained ~~mold~~ **thereby** is irradiated with **a** laser.

In this case, Liquid Crystal Polymer (LCP), polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, ~~Acrylonitrile-Butadiene-Styrene~~ **acrylonitrile-butadiene-styrene** (ABS), polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone, polyimide, epoxy resin, or a composite resin thereof or the like can be used as the polymeric material.

A glass filler, ceramic particles or the like can be mentioned as the inorganic filler. It is preferable that 10-50 weight % of fibers having a diameter ϕ of 1-20 μm and a length of 10 μm or longer or particles having a diameter ϕ of 0.5-20 μm are added to the polymeric material because debris can be further prevented from scattering.

As the laser, an excimer laser (wavelength $\lambda = 193$ nm, 248 nm, 318 nm, 351 nm), a second higher harmonic YAG laser (wavelength $\lambda = 532$ nm), a third higher harmonic YAG laser (wavelength $\lambda = 355$ nm) or the like having a wavelength of 600 nm or shorter can be used.

When the total energy inputted by the laser is 10-500 J/cm^2, the charging state of the laser irradiated region can be suitable for attachment of noble metal.

In particular, laser irradiation conditions such as a fluence (energy per unit pulse in a unit area: J/cm^2/pulse) and the number of times of irradiation are preferably set so that a charging state becomes suitable for precipitating noble metal. Specifically, the fluence and the number of times of irradiation of laser can be set to be any value in region A in ~~a~~ **the** graph shown in Fig. 1. Consequently, a charging state of debris generated by abrasion becomes favorable in a laser irradiated region. Deposition of noble metal described later is appropriately performed and thereby the whole surface of the laser irradiated region can be plated.

Subsequently, the mold is immersed in a noble metal aqueous solution. In this case, as a noble metal aqueous solution which can be used, a palladium aqueous solution obtained by dissolving $PdCl_2$ powder, Na_2PdCl_4 powder or $PdCl_2$ powder in ion-exchanging water, a palladium colloidal aqueous solution obtained by mixing palladium chloride, sodium chloride

and polyethylene glycol mono-P-nonylphenylether, borated nonylphenyl ether and the like can be mentioned.

Thus, according to the above-described pretreatment method, noble metal can be deposited only on the laser irradiated region of a mold. When electroless plating is performed thereafter, an electroless plating film is formed only in this region.

When the polymeric material is two or more kinds of resins having different laser ablation threshold values, irregularities of a laser irradiated region can be made even larger and thereby plating can be formed in a state **such** that peeling is even more difficult.

The pretreatment method for electroless plating according to the present invention will be described in more detail below with reference to examples.

(Example 1)

LCP was used as a polymeric material. As an inorganic filler, 30 weight % of a glass filler having a diameter ϕ of 10 μm was added to this material. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.2 J/cm^2 /pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in a palladium colloidal solution obtained by mixing palladium chloride, sodium chloride and polyethylene glycol mono-P-nonylphenylether and borated nonylphenylether for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating couldn't be obtained by the ~~processings~~ **processing** under the same conditions.

(Example 2)

PES was used as a polymeric material. 30 weight % of a glass filler having a diameter ϕ of 10 μm as an inorganic filler was added to this material. Subsequently, nickel electroless

plating could be attached to the laser irradiated region by processing this under the same conditions as in Example 1. It is noted that when an inorganic filler was not added to PES, plating couldn't be obtained by the ~~processings~~ **processing** under the same conditions.

(Example 3)

PC was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter ϕ of 10 μm was added. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.4 J/cm^2 /pulse, the number of times of irradiation is 1000 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 30 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 30 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region.

(Example 4)

LCP was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter ϕ of 10 μm was added. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a third harmonic YAG laser under conditions that the fluence is 0.5 J/cm^2 /pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 10 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating ~~couldn't~~ **could** **not** be obtained by ~~the processings~~ **processing** under the same conditions.

In the Claims:

Amend claims 1-8 as follows:

1. (Amended) A pretreatment method for electroless plating, ~~wherein~~ **comprising:**

adding an inorganic ~~is added~~ **filler to** a polymeric material;

~~an obtained~~ **molding the material to obtain a** polymeric mold ~~is irradiated;~~

irradiating the mold with a laser; and

~~immersed in an anionic~~ **immersing the mold in a** noble metal aqueous solution.

2. (Amended) The pretreatment method for electroless plating according to ~~Claim~~ **claim** 1, wherein 10-50 weight % of the inorganic filler is added.

3. (Amended) The pretreatment method for electroless plating according to ~~of Claim~~ **claim** 1 or 2, wherein a total energy inputted by the laser **to the mold** is 10-500 J/cm^2.

4. (Amended) The pretreatment method for electroless plating according to ~~any of Claims 1 to 3~~ **claim 1 or 2**, wherein the laser is irradiated **on an area of the mold** so that a fluence and the number of times of irradiation are set to obtain a charging state suitable for precipitating noble metal **on the irradiated area**.

5. (Amended) The pretreatment method for electroless plating according to ~~any of Claims 1 to 4~~ **claim 1 or 2**, wherein the polymeric material is ~~LCP~~ **selected from the group consisting of a liquid crystal polymer**, polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, ABS, polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone, polyimide, epoxy resin ~~or a~~ **and** composite ~~resin~~ **resins** thereof.

6. (Amended) The pretreatment method for electroless plating according to ~~any of Claims 1 to 5~~ **claim 1 or 2**, wherein the polymeric material ~~is composed of~~ **comprises** two or more kinds of resins having different laser ablation threshold values.

7. (Amended) The pretreatment method for electroless plating according to ~~any of Claims 1 to 6~~ **claim 1 or 2**, wherein a palladium aqueous solution is used as the noble metal aqueous solution.

8. (Amended) The pretreatment method for electroless plating according to ~~any of Claims 1 to 7~~ **claim 1 or 2**, wherein a glass filler is used as the inorganic filler.

ABSTRACT OF THE DISCLOSURE

An inorganic filler is added to a polymeric material. An obtained polymeric mold is irradiated with a laser and immersed in a noble metal aqueous solution and thereafter electroless plating is performed.

PRETREATMENT METHOD FOR ELECTROLESS PLATING

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a pretreatment method for electroless plating.

Description of the Related Art:

In general, a surface of a mold composed of a polymeric material is roughened by chemicals, palladium is adsorbed therein and then the mold is subjected to electroless plating. However, since adsorption of palladium alone is difficult, a tin-palladium compound is adsorbed and then reduced.

Surface roughening by using chemicals cannot be selectively performed. When only a prescribed region is plated, the whole surface is once plated and then exposure and development need to be performed by using a photoresist. Therefore, a method by which a surface of a polymeric mold can be easily plated is being required.

As described in Japanese Unexamined Patent Publication No. Hei 4-183873, a method by which a prescribed region can be plated by irradiating a mold composed of a polymeric material with ultraviolet laser beams was proposed. According to this method, only a prescribed region can be plated by irradiating with an ultraviolet laser, immersing in a palladium colloidal aqueous solution and then performing electroless plating. That is, since only an irradiated region is positively charged by the irradiation with an ultraviolet laser, palladium colloid can be easily attached to only the irradiated region when the mold is immersed in an anionic noble metal aqueous solution. Only palladium, which is a

catalyst of electroless plating, can be deposited by allowing the aqueous solution to contain a reducing agent therein.

However, this method using laser irradiation has the following problems and is not employed currently.

First, since only the periphery of the irradiated region (prescribed region) is charged when the laser having a high fluence is irradiated onto it, irradiation of a low fluence needs to be performed. However, a sufficient quantity of charge is not obtained with such irradiation and thereby palladium colloid is not sufficiently attached. A substantial amount of laser beams need to be irradiated and operability is deteriorated. Specifically, when a laser having a low fluence of 0.05 J/cm^2/pulse is irradiated, the number of times of irradiation needs to be 1000 to obtain a sufficient charge quantity.

Also, when a laser having a low fluence is irradiated, surface irregularities of the irradiated region become small and thereby formed plating is easily peeled.

Furthermore, a charging phenomenon by irradiation of a low fluence is unique to the ultraviolet laser and therefore selectable equipment is limited.

Accordingly, a feature of the present invention is to provide a pretreatment method for electroless plating by which a prescribed region can be efficiently and firmly plated irrespective of the kind of a laser.

SUMMARY OF THE INVENTION

The present inventors found that the main cause of charging of a mold surface by laser irradiation was removed and scattered substances (hereinafter, referred to as

debris) generated by abrasion. Also, the present inventors found that these debris could be prevented from scattering by allowing the mold to contain an inorganic filler.

According to the present invention, a pretreatment method for electroless plating as means for solving the aforementioned problems is provided such that an inorganic filler is added to a polymeric material and an obtained polymeric mold is irradiated with a laser and immersed in a noble metal aqueous solution.

With this arrangement, the added inorganic filler generates a sufficient quantity of charged debris upon laser irradiation irrespective of the level of the fluence and the debris are prevented from scattering outside the irradiated region. Therefore, when the mold is immersed in a noble metal aqueous solution, noble metal can attach only to a laser irradiated region. As a result, when electroless plating is performed, noble metal attached to the laser irradiated region acts as a catalyst and thereby a favorable plating film can be formed on a desired site (irradiated region).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a state of an irradiated region depending on the fluence and the number of times of irradiation.

DETAILED DESCRIPTION OF THE INVENTION

An embodiment of the pretreatment method for electroless plating according to the present invention is described below.

In this pretreatment method for electroless plating,

an inorganic filler is added to a polymeric material and the mold obtained thereby is irradiated with a laser.

In this case, Liquid Crystal Polymer (LCP), polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, acrylonitrile-butadiene-styrene (ABS), polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone, polyimide, epoxy resin, or a composite resin thereof or the like can be used as the polymeric material.

A glass filler, ceramic particles or the like can be mentioned as the inorganic filler. It is preferable that 10-50 weight % of fibers having a diameter ϕ of 1-20 μm and a length of 10 μm or longer or particles having a diameter ϕ of 0.5-20 μm are added to the polymeric material because debris can be further prevented from scattering.

As the laser, an excimer laser (wavelength λ = 193 nm, 248 nm, 318 nm, 351 nm), a second higher harmonic YAG laser (wavelength λ = 532 nm), a third higher harmonic YAG laser (wavelength λ = 355 nm) or the like having a wavelength of 600 nm or shorter can be used.

When the total energy inputted by the laser is 10-500 J/cm^2, the charging state of the laser irradiated region can be suitable for attachment of noble metal.

In particular, laser irradiation conditions such as a fluence (energy per unit pulse in a unit area: $J/cm^2/pulse$) and the number of times of irradiation are preferably set so that a charging state becomes suitable for precipitating noble metal. Specifically, the fluence and the number of times of irradiation of laser can be set to be any value in region A in the graph shown in Fig. 1. Consequently, a

charging state of debris generated by abrasion becomes favorable in a laser irradiated region. Deposition of noble metal described later is appropriately performed and thereby the whole surface of the laser irradiated region can be plated.

Subsequently, the mold is immersed in a noble metal aqueous solution. In this case, as a noble metal aqueous solution which can be used, a palladium aqueous solution obtained by dissolving $PdCl_2$ powder, Na_2PdCl_4 powder or $PdCl_2$ powder in ion-exchanging water, a palladium colloidal aqueous solution obtained by mixing palladium chloride, sodium chloride and polyethylene glycol mono-P-nonylphenylether, borated nonylphenyl ether and the like can be mentioned.

Thus, according to the above-described pretreatment method, noble metal can be deposited only on the laser irradiated region of a mold. When electroless plating is performed thereafter, an electroless plating film is formed only in this region.

When the polymeric material is two or more kinds of resins having different laser ablation threshold values, irregularities of a laser irradiated region can be made even larger and thereby plating can be formed in a state such that peeling is even more difficult.

The pretreatment method for electroless plating according to the present invention will be described in more detail below with reference to examples.

(Example 1)

LCP was used as a polymeric material. As an inorganic filler, 30 weight % of a glass filler having a

diameter ϕ of 10 μm was added to this material. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.2 J/cm^2/pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in a palladium colloidal solution obtained by mixing palladium chloride, sodium chloride and polyethylene glycol mono-P-nonylphenylether and borated nonylphenylether for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating couldn't be obtained by the processing under the same conditions.

(Example 2)

PES was used as a polymeric material. 30 weight % of a glass filler having a diameter ϕ of 10 μm as an inorganic filler was added to this material. Subsequently, nickel electroless plating could be attached to the laser irradiated region by processing this under the same conditions as in Example 1. It is noted that when an inorganic filler was not added to PES, plating couldn't be obtained by the processing under the same conditions.

(Example 3)

PC was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter ϕ of 10 μm was added. Then, this material was subjected to

injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.4 J/cm^2/pulse, the number of times of irradiation is 1000 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 30 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 30 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region.

(Example 4)

LCP was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter ϕ of 10 μm was added. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a third harmonic YAG laser under conditions that the fluence is 0.5 J/cm^2/pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 10 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating could not be obtained by processing under the same conditions.

CLAIMS

1. A pretreatment method for electroless plating, comprising:

adding an inorganic filler to a polymeric material;

molding the material to obtain a polymeric mold;

irradiating the mold with a laser;

and

immersing the mold in a noble metal aqueous solution.

2. The pretreatment method for electroless plating according to claim 1, wherein 10-50 weight % of the inorganic filler is added.

3. The pretreatment method for electroless plating according to claim 1 or 2, wherein a total energy inputted by the laser to the mold is 10-500 J/cm^2.

4. The pretreatment method for electroless plating according to claim 1 or 2, wherein the laser is irradiated on an area of the mold so that a fluence and the number of times of irradiation are set to obtain a charging state suitable for precipitating noble metal on the irradiated area.

5. The pretreatment method for electroless plating according to claim 1 or 2, wherein the polymeric material is selected from the group consisting of a liquid crystal polymer, polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, ABS, polyphenylene sulfide, polyetherimide, polyetherether

ketone, polysulfone, polyimide, epoxy resin and composite resins thereof.

6. The pretreatment method for electroless plating according to claim 1 or 2, wherein the polymeric material comprises two or more kinds of resins having different laser ablation threshold values.

7. The pretreatment method for electroless plating according to claim 1 or 2, wherein a palladium aqueous solution is used as the noble metal aqueous solution.

8. The pretreatment method for electroless plating according to claim 1 or 2, wherein a glass filler is used as the inorganic filler.

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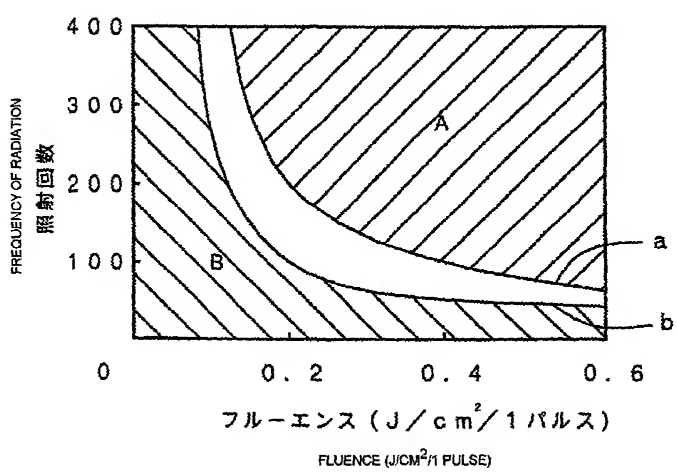
(54) Title: METHOD FOR PRELIMINARY TREATMENT OF MATERIAL TO BE SUBJECTED TO ELECTROLESS PLATING

(54) 発明の名称: 無電解めっきの前処理方法



(57) Abstract: A method for the preliminary treatment of a material to be subjected to electroless plating, characterized in that a polymer material is mixed with an inorganic filler, a formed product obtained from the resultant mixture is immersed in an anionic aqueous solution containing a noble metal. A formed product having been immersed as mentioned above is then subjected to electroless plating.

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TRANSLATION OF JAPANESE SPECIFICATION
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DESCRIPTION

PRETREATMENT METHOD FOR ELECTROLESS PLATING

TECHNICAL FIELD

The present invention relates to a pretreatment method for electroless plating.

BACKGROUND ART

In general, a surface of a mold composed of a polymeric material is roughened by chemicals, palladium is adsorbed therein and then the mold is subjected to electroless plating. However, since adsorption of palladium alone is difficult, a tin-palladium compound is adsorbed and then reduced.

Surface roughening by using chemicals cannot be selectively performed. When only a prescribed region is plated, the whole surface is once plated and then exposure and development need to be performed by using a photoresist. Therefore, a method by which a surface of a polymeric mold can be easily plated is being required.

As described in Japanese Patent Unexamined Publication No. Hei 4-183873, a method by which a prescribed region can be plated by irradiating a mold composed of a polymeric material with ultraviolet laser

beams was proposed.

According to this method, only a prescribed region can be plated only by irradiating with an ultraviolet laser, immersing in a palladium colloidal aqueous solution and then performing electroless plating. That is, since only an irradiated region is positively charged by the irradiation with an ultraviolet laser, palladium colloid can be easily attached to only the irradiated region when the mold is immersed in an anionic noble metal aqueous solution. Only palladium, which is a catalyst of electroless plating, can be deposited by allowing the aqueous solution to contain a reducing agent therein.

However, this method by laser irradiation has the following problems and is not employed currently.

That is, since only the periphery of the irradiated region (prescribed region) is charged when the laser having a high fluence is irradiated, irradiation of a low fluence needs to be performed. However, a sufficient quantity of charge is not obtained with such irradiation and thereby palladium colloid is not sufficiently attached. A substantial amount of laser beams need to be irradiated and operatability is deteriorated. Specifically, when a laser having a low fluence of 0.05 J/cm^2/pulse is irradiated, the number of times of irradiation needs to be 1000 to obtain a sufficient charge quantity.

Also, when a laser having a low fluence is irradiated, surface irregularities of the irradiated region become small and thereby formed plating is easily peeled.

Furthermore, a charging phenomenon by irradiation of a low fluence is unique to an ultraviolet laser and thereby selectable equipment is limited.

Accordingly, an object of the present invention is to provide a pretreatment method for electroless plating by which a prescribed region can be efficiently and firmly plated irrespective of the kind of a laser.

DISCLOSURE OF THE INVENTION

The present inventors found that the main cause of charging of a mold surface by laser irradiation was removed and scattered substances (hereinafter, referred to as debris) generated by abrasion. Also, the present inventors found that these debris could be prevented from scattering by allowing the mold to contain an inorganic filler.

According to the present invention, a pretreatment method for electroless plating as means for solving the aforementioned problems is provided such that an inorganic filler is added to a polymeric material and an obtained polymeric mold is irradiated with a laser and immersed in a noble metal aqueous solution.

With this constitution, the added inorganic filler

generates a sufficient quantity of charged debris upon laser irradiation irrespective of the level of the fluence and the debris are prevented from scattering outside the irradiated region. Therefore, when the mold is immersed in a noble metal aqueous solution, noble metal can be attached only to a laser irradiated region. As a result, when electroless plating is performed, noble metal attached to the laser irradiated region acts as a catalyst and thereby a favorable plating film can be formed on a desired site (irradiated region).

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a state of an irradiated region depending on the fluence and the number of times of irradiation.

BEST MODE FOR CARRYING OUT THE INVENTION

An embodiment of the pretreatment method for electroless plating according to the present invention is described below.

In this pretreatment method for electroless plating, an inorganic filler is added to a polymeric material and an obtained mold is irradiated with laser.

In this case, Liquid Crystal Polymer (LCP), polyethersulfone, polybutylene terephthalate, polycarbonate,

polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, Acrylonitrile-Butadiene-Styrene (ABS), polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone, polyimide, epoxy resin, or a composite resin thereof or the like can be used as the polymeric material.

A glass filler, ceramic particles or the like can be mentioned as the inorganic filler. It is preferable that 10-50 weight % of fibers having a diameter φ of 1-20 μm and a length of 10 μm or longer or particles having a diameter φ of 0.5-20 μm are added to the polymeric material because debris can be further prevented from scattering.

As the laser, an excimer laser (wavelength λ = 193 nm, 248 nm, 318 nm, 351 nm), a second higher harmonic YAG laser (wavelength λ = 532 nm), a third higher harmonic YAG laser (wavelength λ = 355 nm) or the like having a wavelength of 600 nm or shorter can be used.

When the total energy inputted by the laser is 10-500 J/cm^2, the charging state of the laser irradiated region can be suitable for attachment of noble metal.

In particular, laser irradiation conditions such as a fluence (energy per unit pulse in a unit area: $J/cm^2/pulse$) and the number of times of irradiation are preferably set so that a charging state becomes suitable for precipitating noble metal. Specifically, the fluence and the number of

times of irradiation of laser can be set to be any value in region A in a graph shown in Fig. 1. Consequently, a charging state of debris generated by abrasion becomes favorable in a laser irradiated region. Deposition of noble metal described later is appropriately performed and thereby the whole surface of the laser irradiated region can be plated.

Subsequently, the mold is immersed in a noble metal aqueous solution. In this case, as a noble metal aqueous solution which can be used, a palladium aqueous solution obtained by dissolving $PdCl_2$ powder, Na_2PdCl_4 powder or $PdCl_2$ powder in ion-exchanging water, a palladium colloidal aqueous solution obtained by mixing palladium chloride, sodium chloride and polyethylene glycol mono-P-nonylphenylether, borated nonylphenyl ether and the like can be mentioned.

Thus, according to the above-described pretreatment method, noble metal can be deposited only on the laser irradiated region of a mold. When electroless plating is performed thereafter, an electroless plating film is formed only in this region.

When the polymeric material is two or more kinds of resins having different laser ablation threshold values, irregularities of a laser irradiated region can be made even larger and thereby plating can be formed in a state

that peeling is even more difficult.

The pretreatment method for electroless plating according to the present invention will be described in more detail below with reference to examples.

(Example 1)

LCP was used as a polymeric material. As an inorganic filler, 30 weight % of a glass filler having a diameter φ of 10 μm was added to this material. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.2 J/cm^2/pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in a palladium colloidal solution obtained by mixing palladium chloride, sodium chloride and polyethylene glycol mono-P-nonylphenylether and borated nonylphenylether for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating couldn't be obtained by the processings under the same conditions.

(Example 2)

PES was used as a polymeric material. 30 weight % of a glass filler having a diameter φ of 10 μm as an inorganic filler was added to this material. Subsequently, nickel electroless plating could be attached to the laser irradiated region by processing this under the same conditions as in Example 1. It is noted that when an inorganic filler was not added to PES, plating couldn't be obtained by the processings under the same conditions.

(Example 3)

PC was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter φ of 10 μm was added. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a KrF excimer laser under conditions that the fluence is 0.4 J/cm^2/pulse, the number of times of irradiation is 1000 pulses and the cycle frequency is 50 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 30 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 30 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region.

(Example 4)

LCP was used as a polymeric material. As a inorganic filler, 30 weight % of a glass filler having a diameter φ of 10 μm was added. Then, this material was subjected to injection molding. A surface of the obtained mold was irradiated with laser beams by using a third harmonic YAG laser under conditions that the fluence is 0.5 J/cm^2/pulse, the number of times of irradiation is 200 pulses and the cycle frequency is 10 Hz. Subsequently, the mold was immersed in the same palladium colloidal solution as used in Example 1 for 15 minutes. Subsequently, the mold was washed with ion-exchanging water and immersed in an electroless nickel solution for 15 minutes. Consequently, nickel electroless plating could be attached to the laser irradiated region. It is noted that when an inorganic filler was not added to LCP, plating couldn't be obtained by the processings under the same conditions.

CLAIMS

1. A pretreatment method for electroless plating, wherein

an inorganic filler is added to a polymeric material; and

an obtained polymeric mold is irradiated with laser and immersed in a noble metal aqueous solution.

2. The pretreatment method for electroless plating according to Claim 1, wherein

10-50 weight % of the inorganic filler is added.

3. The pretreatment method for electroless plating according to of Claim 1 or 2, wherein

a total energy inputted by the laser is 10-500 J/cm^2.

4. The pretreatment method for electroless plating according to any of Claims 1 to 3, wherein

the laser is irradiated so that a fluence and the number of times of irradiation are set to obtain a charging state suitable for precipitating noble metal.

5. The pretreatment method for electroless plating according to any of Claims 1 to 4, wherein

the polymeric material is LCP, polyethersulfone, polybutylene terephthalate, polycarbonate, polyphenylene ether, polyphenylene oxide, polyacetal, polyethylene terephthalate, polyamide, ABS, polyphenylene sulfide, polyetherimide, polyetherether ketone, polysulfone,

polyimide, epoxy resin or a composite resin thereof.

6. The pretreatment method for electroless plating according to any of Claims 1 to 5, wherein

the polymeric material is composed of two or more kinds of resins having different laser ablation threshold values.

7. The pretreatment method for electroless plating according to any of Claims 1 to 6, wherein

a palladium aqueous solution is used as the noble metal aqueous solution.

8. The pretreatment method for electroless plating according to any of Claims 1 to 7, wherein

a glass filler is used as the inorganic filler.

ABSTRACT

An inorganic filler is added to a polymeric material. An obtained polymeric mold is irradiated with a laser and immersed in a noble metal aqueous solution and thereafter electroless plating is performed.

Title: Pretreatment Method for Electroless Plating
Hirokazu TANAKA et al
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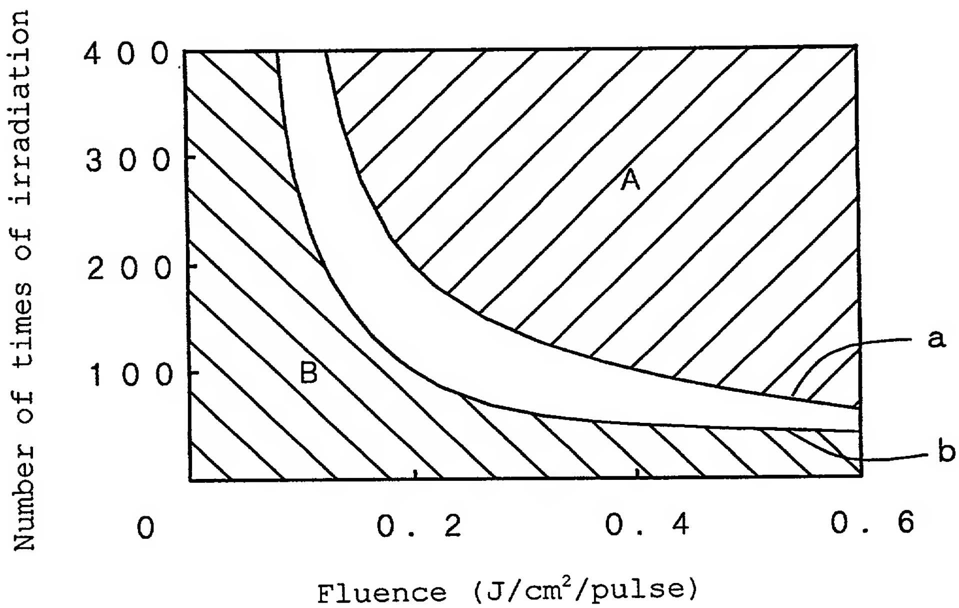
FIG. 1



PATENT
Docket No.

Client Ref.

COMBINED DECLARATION AND POWER OF ATTORNEY FOR UTILITY/DESIGN PATENT APPLICATION

AS A BELOW-NAMED INVENTOR, I HEREBY DECLARE THAT:

My residence, citizenship, and post office address are as stated below next to my name.

I believe I am the original, first and sole (or joint, if more than one name appears below) inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PRETREATMENT METHOD FOR ELECTROLESS PLATING

the specification of which:

☐ is attached hereto.
☒ was filed on July 6, 2000 as International Application No. PCT/JP00/04491

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE.

I acknowledge and understand that I have a duty to disclose information which is material to the patentability of the claims of this application in accordance with Title 37, Code of Federal Reg.ulations, §§ 1.56(a) and (b).

I hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) of the foreign application(s) for patent indicated below and have also identified below the foreign applications for patent or inventor's certificate on this invention having a filing date before that of the application for patent or inventor's certificate on this invention having a filing date before that of the application on which priority is claimed:

Country/International	Application No.	Date of Filing (day/month/year)	Priority Claimed?
			☐Yes ☐No.
			☐Yes ☐No.
			☐Yes ☐No.
			☐Yes ☐No.
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I hereby claim benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Application Serial No.	Filing Date

I hereby claim benefit under Title 35, United States Code, § 120 of any United States application(s) listed below, and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §§ 1.56(a) and (b) set forth above which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status
		☐Patented ☐Pending ☐Abandoned
		☐Patented ☐Pending ☐Abandoned
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